PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 15 November 2000 (15.11.00)	
International application No. PCT/EP00/02573	**Applicant's or agent's file reference** F-784 WO
International filing date (day/month/year) 20 March 2000 (20.03.00)	**Priority date** (day/month/year) 19 March 1999 (19.03.99)
Applicant CHARLIER, Yves	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

17 October 2000 (17.10.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Olivia TEFY

Telephone No.: (41-22) 338.83.38

PC

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For Receiving Office use only

PCT/EP 0 0 / 0 2 5 7 3
International Application No.

2 0 MAR 2000 (20. 03. 2000)
International Filing Date

EUROPEAN PATENT OFFICE
PCT INTERNATIONAL APPLICATION
Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference *(if desired) (12 characters maximum)* **F-784 WO**

Box No. I TITLE OF INVENTION

Polypropylene having improved long chain branching.

Box No. II APPLICANT

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

FINA RESEARCH S.A.
ZONE INDUSTRIELLE C
B-7181 SENEFFE (FELUY)
BELGIUM

☐ This person is also inventor

Telephone No.: **32 64 51.41.11**
Facsimile No.: **32 64 51.46.57**
Teleprinter No.:

State *(i.e. country)* of nationality: **BE**
State *(i.e. country)* of residence: **BE**

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

CHARLIER, Yves
Chaussée de Braine-le-Comte, 79
B-1400 Nivelles
BELGIUM

This person is:
☐ applicant only
☒ applicant and inventor
☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(i.e. country)* of nationality: **BE**
State *(i.e. country)* of residence: **BE**

This person is applicant the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: representative ☐ agent ☒ common

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

FINA RESEARCH S.A.
PATENT DEPARTMENT
ZONE INDUSTRIELLE C
B-7181 SENEFFE (FELUY)
Belgium

Telephone No.: **32 64 51.41.11**
Facsimile No.: **32 64 51.46.57**
Teleprinter No.:

☐ Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) *(mark the applicable check-boxes; at least one must be marked)*:

Regional Patent

- [X] AP **ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- [X] EA **Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- [X] EP **European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- [X] OA **OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT *(if other kind of protection or treatment desired, specify on dotted line)* .....

National Patent *(if other kind of protection or treatment desired, specify on dotted line)*:

- [X] AE United Arab Emirates
- [X] AL Albania
- [X] AM Armenia
- [X] AT Austria
- [X] AU Australia
- [X] AZ Azerbaijan
- [X] BA Bosnia and Herzegovina
- [X] BB Barbados
- [X] BG Bulgaria
- [X] BR Brazil
- [X] BY Belarus
- [X] CA Canada
- [X] CH and LI Switzerland and Liechtenstein
- [X] CN China
- [X] CR Costa Rica
- [X] CU Cuba
- [X] CZ Czech Republic
- [X] DE Germany
- [X] DK Denmark
- [X] DM Dominica
- [X] EE Estonia
- [X] ES Spain
- [X] FI Finland
- [X] GB United Kingdom
- [X] GD Grenada
- [X] GE Georgia
- [X] GH Ghana
- [X] GM Gambia
- [X] HR Croatia
- [X] HU Hungary
- [X] ID Indonesia
- [X] IL Israel
- [X] IN India
- [X] IS Iceland
- [X] JP Japan
- [X] KE Kenya
- [X] KG Kyrgyzstan
- [X] KP Democratic People's Republic of Korea
- [X] KR Republic of Korea
- [X] KZ Kazakhstan
- [X] LC Saint Lucia
- [X] LK Sri Lanka
- [X] LR Liberia
- [X] LS Lesotho
- [X] LT Lithuania
- [X] LU Luxembourg
- [X] LV Latvia
- [X] MA Morocco
- [X] MD Republic of Moldova
- [X] MG Madagascar
- [X] MK The former Yugoslav Republic of Macedonia
- [X] MN Mongolia
- [X] MW Malawi
- [X] MX Mexico
- [X] NO Norway
- [X] NZ New Zealand
- [X] PL Poland
- [X] PT Portugal
- [X] RO Romania
- [X] RU Russian Federation
- [X] SD Sudan
- [X] SE Sweden
- [X] SG Singapore
- [X] SI Slovenia
- [X] SK Slovakia
- [X] SL Sierra Leone
- [X] TJ Tajikistan
- [X] TM Turkmenistan
- [X] TR Turkey
- [X] TT Trinidad and Tobago
- [X] TZ United Republic of Tanzania
- [X] UA Ukraine
- [X] UG Uganda
- [X] US United States of America
- [X] UZ Uzbekistan
- [X] VN Viet Nam
- [X] YU Yugoslavia
- [X] ZA South Africa
- [X] ZW Zimbabwe

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

- [ ] .....
- [ ] .....

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. *(Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)*

 PCT/EP 00 / 02573

Box No. VI PRIORITY CLAIM Further priority claims are indicated in the Supplemental Box ☐

The priority of the following earlier application(s) is hereby claimed:

Country *(in which, or for which, the application was filed)*	Filing Date *(day/month/year)*	Application No.	Office of filing *(only for regional or international application)*
item (1) ~~EP~~ BE	(19. 03. 1999) 19 MAR 1999	99105661.5	EP
item (2)			
item (3)			

RO/E

Mark the following check-box if the certified copy of the earlier application is to be issued by the Office which for the purposes of the present international application is the receiving Office (a fee may be required):

[X] The receiving Office is hereby requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s) : 1

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) *(If two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):* ISA /_____

Earlier search *Fill in where a search (international, international-type or other) by the International Searching Authority has already been carried out or requested and the Authority is now requested to base the international search to the extent possible, on the results of that earlier search. Identify such search or request either by reference to the relevant application (or the translation thereof) or by reference to the search request*

Country (or regional Office): **EP** Date *(day/month/year)*:**02.09.1999** Number: **99105661.5**

Box No. VIII CHECK LIST

This international application contains the following number of sheets:

1. request	3	sheets
2. description	16	sheets
3. claims	2	sheets
4. abstract	1	sheets
5. drawings	1	sheets
Total :	23	sheets

This international application is accompanied by the item(s) marked below:

1. ☐ separate signed power of attorney
2. [X] copy of general power of attorney **JCD/FL/MCR**
3. ☐ statement explaining lack of signature
4. ☐ priority document(s) *identified in Box No VI as item(s):*
5. ☐ fee calculation sheet
6. ☐ separate indications concerning deposited microorganisms
7. ☐ nucleotide and/or amino acid sequence listing (diskette)
8. [X] other *(specify):Earlier Search*

Figure No. of the drawings (if any) should accompany the abstract when it is published.

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request)

TINA RESEARCH S.A.

LEYDER, Francis (GA 23919)

For receiving Office use only

1. Date of actual receipt of the purported international application:	20 MAR 2000 (20. 03. 2000)	2. Drawings: [X] received ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority specified by the applicant: ISA/	6. ☐ Transmittal of search copy delayed until search fee is paid	

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

INTERNATIONAL SEARCH REPORT

Inte .ional Application No
PCT/EP 00/02573

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F255/02 C08G81/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 821 018 A (DANUBIA PETROCHEM POLYMERE) 28 January 1998 (1998-01-28) page 8, line 33-37; claims 1-3; example 15 ---	1
A	US 5 605 936 A (FELLONI MASSIMO ET AL) 25 February 1997 (1997-02-25) cited in the application page 8, line 24-42 ---	1
A	EP 0 519 341 A (HIMONT INC) 23 December 1992 (1992-12-23) example 2 ---	1
A	EP 0 520 773 A (SEKISUI CHEMICAL CO LTD) 30 December 1992 (1992-12-30) cited in the application page 5, line 11; example 1 ---	1

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 August 2000	10/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Meulemans, R

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Int ational Application No
PCT/EP 00/02573

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 411 994 A (GALLI PAOLO ET AL) 2 May 1995 (1995-05-02) column 5, line 64 -column 6, line 17; example 1	1
A	EP 0 792 905 A (DANUBIA PETROCHEM POLYMERE) 3 September 1997 (1997-09-03) claim 1	1

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

RNATIONAL SEARCH REPORT

Information on patent family members

Inte ional Application No
PCT/EP 00/02573

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0821018 A	28-01-1998	DE 19629429 A	29-01-1998
		DE 19629427 A	29-01-1998
US 5605936 A	25-02-1997	US 5541236 A	30-07-1996
		US 5414027 A	09-05-1995
		AT 166368 T	15-06-1998
		CA 2128064 A	16-01-1995
		CN 1105033 A	12-07-1995
		DE 69410357 D	25-06-1998
		DE 69410357 T	08-10-1998
		EP 0634441 A	18-01-1995
		JP 7138430 A	30-05-1995
		MX 9405377 A	31-01-1995
EP 0519341 A	23-12-1992	AT 141297 T	15-08-1996
		AU 1829692 A	24-12-1992
		BR 9202326 A	19-01-1993
		CA 2071650 A	22-12-1992
		CN 1069036 A,B	17-02-1993
		CZ 9201908 A	17-02-1993
		DE 69212722 D	19-09-1996
		DE 69212722 T	23-01-1997
		DK 519341 T	02-09-1996
		FI 922878 A	22-12-1992
		HU 65142 A	28-04-1994
		JP 5178943 A	20-07-1993
		MX 9203003 A	01-02-1993
		NO 922434 A	22-12-1992
		ZA 9204249 A	31-03-1993
EP 0520773 A	30-12-1992	JP 3025057 B	27-03-2000
		JP 5001170 A	08-01-1993
		DE 69207654 D	29-02-1996
		DE 69207654 T	11-07-1996
		US 5304580 A	19-04-1994
US 5411994 A	02-05-1995	US 5652281 A	29-07-1997
		AT 118792 T	15-03-1995
		AU 630534 B	29-10-1992
		AU 6825790 A	27-06-1991
		BR 9006519 A	01-10-1991
		CA 2031406 A	22-06-1991
		CN 1054077 A,B	28-08-1991
		DE 69017184 D	30-03-1995
		DE 69017184 T	29-06-1995
		DK 437808 T	19-06-1995
		EP 0437808 A	24-07-1991
		FI 906310 A	22-06-1991
		HU 59709 A	29-06-1992
		JP 2000026549 A	25-01-2000
		JP 2957709 B	06-10-1999
		JP 6157683 A	07-06-1994
		NO 905525 A	24-06-1991
		PT 96292 A,B	30-09-1991
		KR 169730 B	20-03-1999
		RU 2090574 C	20-09-1997
		ZA 9009902 A	30-10-1991

INTERNATIONAL SEARCH REPORT

Information on patent family members

.ional Application No
PCT/EP 00/02573

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0792905 A	03-09-1997	DE 19607480 A	04-09-1997
		CA 2198651 A	28-08-1997
		JP 9328583 A	22-12-1997
		US 5883151 A	16-03-1999

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
F-784 WO		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP 00/ 02573	20/03/2000	19/03/1999
Applicant		
FINA RESEARCH S.A.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by th applicant.

   [ ] th text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawing** to be published with the abstract is Figure No. _____

   [ ] as suggested by th applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better charact rizes th invention.

   [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
[redacted]/EP 00/02573

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F255/02 C08G81/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 605 936 A (FELLONI MASSIMO ET AL) 25 February 1997 (1997-02-25) cited in the application page 8, line 24-42 ---	1
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A	EP 0 520 773 A (SEKISUI CHEMICAL CO LTD) 30 December 1992 (1992-12-30) cited in the application page 5, line 11; example 1 ---	1
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 August 2000	10/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Meulemans, R

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
[redacted]T/EP 00/02573

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 411 994 A (GALLI PAOLO ET AL) 2 May 1995 (1995-05-02) column 5, line 64 -column 6, line 17; example 1	1
A	EP 0 792 905 A (DANUBIA PETROCHEM POLYMERE) 3 September 1997 (1997-09-03) claim 1	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
/EP 00/02573

Patent document cited in search report		Publication dat	Patent family member(s)		Publication date
EP 0821018	A	28-01-1998	DE	19629429 A	29-01-1998
			DE	19629427 A	29-01-1998
US 5605936	A	25-02-1997	US	5541236 A	30-07-1996
			US	5414027 A	09-05-1995
			AT	166368 T	15-06-1998
			CA	2128064 A	16-01-1995
			CN	1105033 A	12-07-1995
			DE	69410357 D	25-06-1998
			DE	69410357 T	08-10-1998
			EP	0634441 A	18-01-1995
			JP	7138430 A	30-05-1995
			MX	9405377 A	31-01-1995
EP 0519341	A	23-12-1992	AT	141297 T	15-08-1996
			AU	1829692 A	24-12-1992
			BR	9202326 A	19-01-1993
			CA	2071650 A	22-12-1992
			CN	1069036 A,B	17-02-1993
			CZ	9201908 A	17-02-1993
			DE	69212722 D	19-09-1996
			DE	69212722 T	23-01-1997
			DK	519341 T	02-09-1996
			FI	922878 A	22-12-1992
			HU	65142 A	28-04-1994
			JP	5178943 A	20-07-1993
			MX	9203003 A	01-02-1993
			NO	922434 A	22-12-1992
			ZA	9204249 A	31-03-1993
EP 0520773	A	30-12-1992	JP	3025057 B	27-03-2000
			JP	5001170 A	08-01-1993
			DE	69207654 D	29-02-1996
			DE	69207654 T	11-07-1996
			US	5304580 A	19-04-1994
US 5411994	A	02-05-1995	US	5652281 A	29-07-1997
			AT	118792 T	15-03-1995
			AU	630534 B	29-10-1992
			AU	6825790 A	27-06-1991
			BR	9006519 A	01-10-1991
			CA	2031406 A	22-06-1991
			CN	1054077 A,B	28-08-1991
			DE	69017184 D	30-03-1995
			DE	69017184 T	29-06-1995
			DK	437808 T	19-06-1995
			EP	0437808 A	24-07-1991
			FI	906310 A	22-06-1991
			HU	59709 A	29-06-1992
			JP	2000026549 A	25-01-2000
			JP	2957709 B	06-10-1999
			JP	6157683 A	07-06-1994
			NO	905525 A	24-06-1991
			PT	96292 A,B	30-09-1991
			KR	169730 B	20-03-1999
			RU	2090574 C	20-09-1997
			ZA	9009902 A	30-10-1991

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
[redacted]/EP 00/02573

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0792905 A	03-09-1997	DE 19607480 A	04-09-1997
		CA 2198651 A	28-08-1997
		JP 9328583 A	22-12-1997
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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
F-784 WO		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP00/02573	20/03/2000	19/03/1999
International Patent Classification (IPC) or national classification and IPC C08F255/02		
Applicant FINA RESEARCH S.A. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
17/10/2000	14.12.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Simmerl, R Telephone No. +49 89 2399 8515

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/02573

I. Basis of the rep rt

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:
Description, pages:

1-16 as originally filed

Claims, No.:

1-8 as originally filed

Drawings, sheets:

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-8
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-8
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-8
	No:	Claims	

2. Citations and explanations
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
s separate sheet

Ad s ction V.:

1. The subject-matter of the claims is novel (Art. 33(2) PCT) since none of the documents cited in the search report discloses a polypropylene as defined in claim 1 and a process for its preparation.

2. The subject-matter of claims is based on an inventive step (Art. 33(3) PCT).

   It was the problem of the present application to provide a polypropylene having improved long chain branching in combination with improved melt strength, recovery compliance and relaxation time (page 4, second full paragraph).

   The closest prior art document is EP-A-0 821 018. EP deals with the preparation of cross-linkable polyolefins by means of ionizing radiation. The problem of the present application is neither mentioned in EP nor is there any suggestion as regards the combination of features given in present claim 1.

3. Industrial Applicability (Art. 33(4) PCT): o.k.

Ad section VIII.:

1. Independent claim 7 contains all the features of claim 1. With respect to Rule 6.4 a) EPC claim 7 should contain a reference to claim 1.

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[redacted] D INTELLECTUAL PROPERTY ORGANIZATION [redacted]
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(54) Title: POLYPROPYLENE HAVING IMPROVED LONG CHAIN BRANCHING

(57) Abstract

Polypropylene having improved long chain branching increased melt strength obtained by irradiating polypropylene with an electron beam having an energy of at least 5 MeV and with a radiation dose of from 5 to 100 kGray in the presence of a grafting agent, the branching index of the obtained polypropylene being lower than 0.7.

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POLYPROPYLENE HAVING IMPROVED LONG CHAIN BRANCHING

The present invention relates to polypropylene having improved long chain branching particularly such polypropylene presents high melt strength, recovery compliance and/or good relaxation time. The polypropylene with improved long chain branching of the present invention is obtained by irradiating polypropylene with a high energy electron beam in the presence of a grafting agent.

Polypropylene resin is used in a variety of different applications. However, polypropylene resin suffers from the problem of having a low melt strength, which restricts the use of polypropylene in a number of applications because the polypropylene is difficult to process. It is known in the art to increase the melt strength of polypropylene, for example by irradiating the polypropylene with an electron beam. It is known that electron beam irradiation significantly modifies the structure of a polypropylene molecule. The irradiation of polypropylene results in chain scission and grafting (or branching) which can occur simultaneously. Up to a certain level of irradiation dose, it is possible to produce from a linear polypropylene molecule having been produced using a Ziegler-Natta catalyst, a modified polymer molecule having free-end long branches, but the properties are not significantly improved.

For example, US-A-5554668 discloses a process for irradiating polypropylene to increase the melt strength thereof. An increase in the melt strength is achieved by decreasing the melt flow rate, otherwise known as the melt index. It is disclosed that a linear propylene polymer material is irradiated with high energy ionising radiation, preferably an electron beam, at a dose rate in the range of from about 1 to $1x10^4$ Mrads per minute for a period of time sufficient for a substantial amount of chain

scission of the linear, propylene polymer molecule to occur but insufficient to cause gelation of the material. Thereafter, the material is maintained for a period of time sufficient but too long for a significant amount of long chain branches to form. Finally, the material is treated to deactivate substantially all free radicals present in the irradiated material. In addition, the specification discloses the use of a very broad range of dose rates *i.e.* from 1 to $1x10^4$ Mrads per minute. High dose rates of greater than about 40 Mrad can result in a substantially fully cross-linked structure of the polypropylene. Such a cross-linked structure is difficult to process.

CA-A-2198651 discloses a continuous method for producing polypropylene mixtures of increased stress-crack resistance and melt strength in which a low-energy electron beam accelerator with an energy of from 150 to 300 keV at a radiation dose of 0.05 to 12 Mrads is employed. This process also suffers from the disadvantage that the production rate of the irradiated powder can be somewhat low for commercial acceptance. Moreover, the polypropylene powder to be irradiated must be in the form of very fine particles. The specification discloses that bifunctional, unsaturated monomers can be added before and/or during the irradiation. Such compounds may include divinyl compounds, alkyl compounds, dienes, or mixtures thereof. These bifunctional, unsaturated monomers can be polymerised with the help of free radicals during the irradiation. However, no indication is given on how to proceed to improve the long chain branching of the polypropylene.

EP-A-0520773 discloses an expandable polyolefin resin composition including polypropylene optionally blended with polyethylene. In order to prepare a cross-linked foam, a sheet of expandable resin composition is irradiated with ionising radiation to cross-link the resin. The ionising radiation may include electron rays, at a dose of from 1 to 20 Mrad. It is disclosed that auxiliary cross-linking agents may be employed which include a bifunctional monomer, exemplified by 1,9-nonanediol

dimethyacrylate.

US-A-2948666 and US-A-5605936 disclose processes for producing irradiated polypropylene. The latter specification discloses the production of a high molecular weight, non-linear propylene polymer material characterised by high melt strength by high energy irradiation of a high molecular weight linear propylene polymer. It is disclosed that the ionising radiation for use in the irradiation step may comprise electrons beamed from an electron generator having an accelerating potential of 500 to 4000 kV. For a propylene polymer material without a polymerised diene content, the dose of ionising radiation is from 0.5 to 7 Mrad. For propylene polymer material having a polymerised diene content, the dose is from 0.2 to 2 Mrad. But once again, there is no indication on the long chain branching.

EP-A-0821018 discloses the preparation of cross linkable olefinic polymers which have been subjected to ionising radiation. The specification exemplifies electron beams of relatively low energy and low doses to split polymeric chains in order to graft silane derivatives onto the polymeric chain. The specification does not address the problem of achieving high melt strength of polymers.

EP-A-0519341 discloses the grafting of vinyl monomers on particulate olefin polymers by irradiating the polymer and treating thereafter with a grafting monomer. In an example, polypropylene is irradiated with an electron beam having an energy of 2 MeV and subsequently treated with maleic anhydride as a grafting monomer.

US-A-5411994 discloses the production of graft copolymers of polyolefins in which a mass of olefin polymer particles is irradiated and thereafter the mass is treated with a vinyl monomer in liquid form. The ionising radiation dose is about 1 to 12 Mrad and the ionising radiation preferably comprises electrons beamed from an electron generator having an accelerating potential of 500 to 4000 kV. The polymer is first

irradiated and then treated with a grafting agent.

EP-A-0792905 discloses the continuous production of polypropylene mixtures of increased stress crack resistance and melt strength by the action of ionising radiation. The energy of the ionising radiation is from 150 to 300 keV and the radiation dose ranges from 0.05 to 12 Mrad.

The present invention aims to provide polypropylene resins having improved long chain branching as well as improved melt strength. More particularly the branching index of polypropylene of the invention should be lower than 0.7. It is also a goal of the invention to provide a process to prepare polypropylene with substantially increased long chain branching on the polypropylene molecules following the irradiation, while employing relatively low irradiation doses. It is a further aim to produce polypropylene having not only improved long chain branching and improved melt strength, but also improved recovery compliance and relaxation time.

Accordingly, the present invention provides for polypropylene having increased long chain branching particularly having a branching index of lower than 0.7 melt strength. It has been unexpectedly found that such improved long chain branching (LCB) polypropylene may be obtained by irradiating polypropylene with an electron beam having an energy of at least 5 MeV and with a radiation dose of from 5 to 100 kGray in the presence of a grafting agent for forming long chain branches on the polypropylene molecules.

It has also been unexpectedly found that such improved LCB polypropylene may be obtained with high energies owing to the conjoint use of a grafting agent during the irradiation step.

Such improvement has been found and finally measured through the determination of the branching index.

The branching index as mentioned in the present patent application is obtained by the ratio of weight average MW values inferred from rheological measurement at zero shear viscosity and at crossover points as fully described in Polymer Testing 11, 89 (1992) by K. Bernreitner et al.

Preferably, the polypropylene is irradiated at an energy of at least 10 MeV.

The polypropylene may be a homopolymer of propylene or a random or block copolymer of propylene and one or more olefins and/or dienes selected from ethylene and C_4 to C_{10} 1-olefins or dienes, which may be linear or branched. The polypropylene homopolymer may be reinforced by rubber particles, for example ethylene-propylene rubber particles, typically in an amount of up to 30wt%. The polypropylene may be a terpolymer optionally with a diene, for example norbornadiene, as a comonomer.

According to the present invention, the polypropylene to be irradiated is mixed prior to irradiation with the grafting agent which increases the long chain branching of the propylene molecules as a result of the irradiation. The grafting agent is directly incorporated into the propylene molecule during the irradiation step. The grafting agent includes at least one carbon-carbon double bond, and preferably is polyunsaturated, being for example bi, ter or tetra unsaturated. The non-conjugated unsaturated compounds are preferred, although conjugated saturated compounds may be employed. The grafting agent may contain polar groups, such as ester, anhydride, or imide groups and/or non-metallic elements such as silicon, phosphorous and halogen atoms. The grafting agent may be selected from the group consisting of bismaleimide derivatives; mono-, di-, tri-, tetra-acrylate or methacrylate compounds; organosilane compounds of the formula $A_{4-n}SiR_n$ where A are identical or different acrylate or methacrylate or vinyl groups, where R are identical or different alkoxy or acetoxy groups and

where n is 1, 2, 3 or 4; α,β-unsaturated acids and their anhydride derivatives; non-conjugated dienes such as 1,5-hexadiene, norbornadiene and dicyclopentadiene; dipentene; polybutadiene and copolymers containing polybutadiene blocks; butadiene based polymers and copolymers; polyisoprene and copolymers containing polyisoprene blocks; isoprene based polymers and copolymers; polyethylene; C_{4-20} α-olefins either linear or branched; styrene or divinylbenzene; ethylene-propylene rubbers and ethylene-propylene-diene rubbers; di-furnane derivatives; ester derivatives of fatty acids; and vinylpolybutadiene.

A particularly preferred grafting agent comprises tetravinyl silane.

The grafting agent employed in accordance with a preferred aspect of the invention results, following irradiation, in polypropylene molecules having some free end terminations, with a cross-link density which is not so high as to reduce the processability of the polymer.

In a further preferred aspect, functional monomers such as maleic anhydride, styrene, acrylic acid, methacrylic acid, 1,4-butanediol diacrylate, or ethylene glycol dimethacrylate may be incorporated into the polypropylene resin. These functional comonomers promote long chain branching of the polypropylene molecules.

In a particularly preferred embodiment of the invention, polypropylene homopolymer in fluff or powder form in an oxygen-free environment is mixed with a grafting agent. Preferably, the grafting agent comprises from 0.01 to 5 wt% of the weight of the polypropylene, more preferably from 0.01 to 1 wt% of the weight of the polypropylene. A particularly preferred grafting agent comprises tetravinyl silane in an amount of from 0.01 to 1wt% based on the weight of the polypropylene, most particularly from 0.01 to 0.5 wt% based on the weight of the polypropylene.

The polypropylene/grafting agent mixture is thereafter deposited onto a continuously moving conveyor such as an endless belt. The mixture on the conveyor passes under an electron beam generator which irradiates the mixture. The accelerating potential or energy of the electron beam is at least 5 MeV, more preferably from 5 to 100 MeV, still more preferably at least 10 MeV, yet more preferably from 10 to 25 MeV. The power of the electron beam generator is preferably from 50 to 500 kW more preferably for 120 to 250 kW. The radiation dose to which the polypropylene/ grafting agent mixture is subjected is preferably from 10 to 100 kGray, preferably around 15 kGray (10 kGray is equivalent to 1 Mrad). The conveyor speed is adjusted in order to achieve the desired dose. Typically, the conveyor speed is from 0.5 to 20 metres/minute, preferably from 1 to 10 metres/minute, more preferably from 2.25 to 8.5 metres/minute.

As a result of the high irradiating potential of the electron beam, not only can the conveyor speed be significantly higher than in the prior art, but also the thickness of the continuously moving bed of polypropylene/grafting agent mixture on the conveyor can be relatively high. Typically, the bed of polypropylene homopolymer and grafting agent has a thickness of up to 20 cm, most particularly from 5 to 10 cm. The bed of polypropylene homopolymer/grafting agent mixture on the conveyor typically has a width of up to about 1 metre. The irradiation is carried out under an inert atmosphere, such as nitrogen.

After irradiation by the electron beam, the polypropylene powder can be annealed and then treated with at least one known antioxidant additive. The annealing temperature may range from 50 to 150°, more preferably from 80 to 120°C and the annealing time may range from 1 to 60 minutes, more preferably from 5 to 30 minutes. Thereafter the polypropylene is granulated.

In accordance with the invention, the irradiated polypropylene has increased recovery compliance, relaxation time and melt

strength. These particular rheological properties provide an outstanding processing behaviour which allows the polypropylene based polymers produced in accordance with the invention to be suitable particularly for producing films, sheets, fibres, pipes, foams, hollow articles, panels and coatings. The irradiated polypropylene also has improved mechanical properties, such as flexural modulus and impact resistance.

The invention will now be described in greater detail with reference to the following non-limiting example and the accompanying drawing, in which:-

Figure 1 is a graph showing the relationship between melt strength and temperature for high melt strength polypropylene produced in accordance with an embodiment of the process of the invention and two other polypropylenes not produced in accordance with the invention.

EXAMPLE

In accordance with the example, a polypropylene homopolymer fluff in the form of a powder having a median particle size (d_{50}) of from 1000 to 1500 microns, a bulk density of around 0.5g/cc and having a melt flow index (MFI) of 1.0 g/10min was treated by irradiation. In this specification the melt flow index (MFI) is measured by the procedure of ASTM D 1238 using a load of 2.16kg at a temperature of 230°C. The polypropylene powder had been treated under pure nitrogen since the presence of oxygen is detrimental to the irradiation process.

The polypropylene powder was then mixed with a grafting agent comprising tetravinyl silane in an amount of 0.5wt% based on the weight of the polypropylene powder. Thereafter, the mixture of the polypropylene powder and the grafting agent was subjected to electron beam irradiation.

In particular, the polypropylene powder and grafting agent mixture was deposited onto an endless belt conveyor having a

speed of 8.5 metres per minute. The polypropylene powder/grafting agent mixture was deposited onto the conveyor as a 1 metre wide bed having a thickness of 7 cm. The conveyor conveyed the bed underneath a high energy high power electron accelerator. Such accelerators are available in commerce. The accelerator had an energy of 10 MeV and a power of 120 kW. The polypropylene powder/grafting agent mixture was irradiated for a period of time (determined by the conveyor speed) sufficient to provide a radiation dose of 15 kGray. During the irradiation, the powder was maintained under nitrogen to exclude oxygen.

After irradiation, the powder was mixed with conventional antioxidant additives. Thereafter, the powder was granulated under nitrogen gas.

In order to demonstrate the benefits of the present invention, a number of samples were tested to determine their properties, with one of the samples being processed in accordance with the method of the present invention, and the remaining samples not being processed in accordance with the method of the present invention. Thus referring to Table 1, seven samples, with their respective treatments, are indicated.

Sample 3 corresponds to the above-described Example in which the specified polypropylene resin was irradiated by the electron beam at the dose and conveyor speed specified in Table 1, with the polypropylene having being mixed with tetravinyl silane grafting agent prior to irradiation.

The remaining samples 1, 2 and 4 to 7 are not in accordance with the invention but are included so as to show comparatively the benefits of the invention exemplified by sample 3.

Sample 1 corresponds to the same polypropylene as employed for sample 3, but which was not irradiated; in other words it was the original polypropylene material.

Sample 2 corresponds to the same polypropylene material which was subjected to irradiation under the dose and conveyor speed specified in Table 1, with the polypropylene not having been mixed with a grafting agent prior to irradiation.

Sample 4 corresponds to the same polypropylene which was subjected to the same irradiation treatment as sample 2, but then the polypropylene was annealed after the irradiation step to facilitate recombination of any remaining radicals. The annealing temperature was 120° and the annealing time was 30 minutes.

For each of samples 2 and 4, it may be seen that the dose of irradiation is significantly higher than that for sample 3 in accordance with the invention, and that the conveyor speed is significant lower than that for sample 3 of the invention. This is because in the absence of a grafting agent, in order to achieve a reasonable level of branching following irradiation, not only must the dose be very high but also the conveyor speed must be considerably lower in order to increase the irradiation time to ensure that a reasonable level of branching is achieved. This significantly reduces the production rate of the irradiated polypropylene. The higher dose required for samples 2 and 4 increases the production costs.

In Table 1, samples 5, 6 and 7 correspond to three respective commercially available polypropylene resins with melt flow index of around 3g/10 min. Profax PF 184 is available in commerce from the company Montell North America, Inc. of Wilmington, Delaware, United States of America and comprises a polypropylene homopolymer which has been irradiated by a low density electron beam at a high irradiation dose. The product Daploy 130 D is a polypropylene resin available in commerce from the company PCD Polymere GmbH of Schwechat-Mannsworth, Austria. The product FINAPRO PPH 4060 is a polypropylene resin available in commerce from the company Fina Chemicals of Belgium. Samples 5 and 6 are high melt strength polypropylene resins with long chain branching

and sample 7 is a linear polypropylene homopolymer.
The branching index has been measured for all the samples and it can be seen from Table 1 the significant improvement in the long chain branching of the polypropylene of the invention.

By way of information, a linear polymer has a branching index of about 1 while a branched polymer presents a branching index lower than 1.

Referring to Table 2, the melt flow index (MFI) of each of the seven samples was measured. It will be seen that sample 3, corresponding to the polypropylene produced in accordance with the method of the present invention, had the lowest melt flow index of 0.86 g/10min. This demonstrates that the use of grafting agent promotes the recombination of macroradicals and reduces the incidence of chain scission when compared to samples 2 and 4.

The MFI of sample 1 was increased by irradiation to form sample 2 as a result of chain scission caused by the radiation.

When a grafting agent is not used, there is no improvement at all for the long chain branching.

For samples 1 to 6 the mechanical properties of extrusion force at 250°C, melt strength at 250°C, 270°C and 290°C and speed at break 250°C, 270°C and 290°C were measured and the results are shown in Table 3. The melt strength is the force, measured in milliNewtons (mN) that is required to draw a polymer in the molten state. In this specification, the melt strength has been measured using a rheological device for capillary and tensile rheometry on polymer melts, such as a CEAST 1000 rheometer. In this specification, the polymer is melted and extruded through a capillary die. The extrusion force, or the force which is applied to the melt to be extruded through the capillary die at a constant flow rate, is measured in newtons (N). The filament is drawn by stretching or elongation as a result of being

attached to a roll which is rotating with a constant acceleration of 10 rpm per 100 seconds, with an initial rotational speed of 2 rpm. The force required to draw the filament is recorded continuously and is expressed in milliNewtons (mN). The force increases with an increase in the rotational speed of the roll until the force reaches a plateau, which is recorded as the final value of the melt strength. It is this final value which is specified in Table 3. Additionally, the rotational speed at which the filament breaks is also determined and is expressed as an instantaneous rotational speed in rpm and corresponds to the speed at break specified in Table 3. It may be seen that for sample 3 produced in accordance with the invention, this shows a high level of melt strength, particularly over a range of processing temperatures and rather a low speed at break. Samples 5 and 6 lose their melt strength at 290°C and are spinnable as a standard product. At 290°C sample 3 has a good level of melt strength. In contrast, samples 2 and 4 show a limited increase of melt strength.

Figure 1 shows for samples 3, 5 and 6 the relationship between melt strength and temperature. It may be seen that for sample 3, as compared to samples 5 and 6, the rate of decrease of melt strength of temperature is significantly reduced. Moreover, it may also be seen that the polypropylene of sample 3 still has a high melt strength at 290°C, while the polypropylenes of samples 5 and 6 have no significant melt strength at that temperature. Thus the process of the present invention enables the production of high melt strength polypropylenes which have good melt strength at high temperatures, enabling them to be processed, for example to produce spun fibres, at high processing temperatures.

It may be thus seen in accordance with the invention that the use of the process of the invention can provide a polypropylene having a high melt strength which is a strong advantage when the molten polymer is being processed, for example when being blown into film, extruded into pipes, spun into fibres, or formed as

a foam.

Referring to Table 4, this shows the values of the flexural modulus and the impact resistance for sample 3 produced in accordance with the invention, and for samples 1, 5, 6 and 7. The flexural modulus was measured using the procedure of ISO 178 and the impact resistance was measured using the IZOD test at 23°C of the procedure of ISO R180/1A. Comparing the polypropylene of sample 3 with that of sample 1, it may be seen that the use of high energy electron beam irradiation in combination with the grafting agent for forming long chain branches on the polypropylene molecules increases both the flexural modulus and the impact resistance of the polypropylene, while keeping substantially the same melt flow index. The mechanical properties of the polypropylene are improved, while maintaining substantially the same melt flow properties of the polypropylene. Comparing the polypropylene of sample 3 produced in accordance with the invention with those of samples 5, 6 and 7 which are commercially available polypropylenes, it may be seen that the flexural modulus of the polypropylene produced in accordance with the invention is either the same as or significantly greater than the flexural modulus of those known commercial polypropylenes, and also compared to all three samples 5, 6 and 7 sample 3 has a significantly higher impact resistance, for example at least about 50% higher than for the known polypropylene. Thus the process of the present invention enables a polypropylene having improved mechanical properties, as well as increased melt strength, to be achieved.

The recovery compliance and relaxation time were measured for samples 1 to 7 and the results are shown in Table 5. In accordance with the invention the recovery compliance and relaxation times of sample 3 are higher than that for samples 2 and 4 where no grafting agent was employed. Moreover, for sample 3 produced in accordance with the invention, the relaxation time was significantly higher than that for all the other samples. These results clearly show the advantage of adding a grafting agent prior to the irradiation step.

TABLE 1

Sample	Treatment	Dose (kGray)	Conveyor Speed (m/min)	Branching Index
1	Non-irradiated PP	-	-	-
2	Irradiated PP	60	2.1	0.89
3	Irradiated PP in the presence of a grafting agent	15	8.5	0.52
4	Irradiated PP and annealed	60	2.1	0.83
5	Profax PF 814	Not Known	Not Known	0.72
6	Daploy 130 D	Not Known	Not Known	0.7
7	FINAPRO PPH 4060 non-irradiated	-	-	1.01

TABLE 2

Sample	MFI (g/10')
1	1.0
2	3.0
3	0.86
4	4.0
5	3.1
6	2.98
7	3.0

TABLE 3

Sample	Extrusion force (daN)	Melt strength (mN)			Speed at break (rpm)		
		250°C	270°C	290°C	250°C	270°C	290°C
1	8	8	-	-	>240	-	-
2	3	17	-	-	35	-	-
3	8	45	35	15	3	3	3
4	3	17.5	-	-	35	-	-
5	3	50	20	1.5	9	25	170
6	-	-	40	2	-	5	-

TABLE 4

Sample	Flexural modulus (MPa)	Impact resistance (kJ/m^2)
1	1615	4.5
3	1955	7.3
5	1685	3.2
6	2020	5.5
7	1360	4.8

TABLE 5

Sample	Recovery Compliance ($1x10^{-4}/Pa$)	Relaxation Time (sec)
1	3.1	6.5
2	12.0	10.6
3	29.4	106.0
4	11.7	10.9
5	35.2	15.0
6	49.8	28.3
7	5.5	2.9

CLAIMS:

1. Polypropylene having improved long chain branching and increased melt strength characterized in that it is produced by irradiating polypropylene with an electron beam having an energy of at least 5 MeV with a radiation dose of from 5 to 100 kGray in the presence of a grafting agent.

2. A polypropylene according to claim 1 wherein the electron beam energy to be used is of at least 10 MeV.

3. A polypropylene according to claim 1 or 2 wherein the grafting agent is selected from the group consisting of bismaleimide derivatives; mono-, di-, tri-, tetra-acrylate or methacrylate compounds; organosilane compounds of the formula $A_{4-n}SiR_n$ where A are identical or different acrylate or methacrylate or vinyl groups, where R are identical or different alkoxy or acetoxy groups and where n is 1, 2, 3 or 4; α,β-unsaturated acids and their anhydride derivatives; non-conjugated dienes such as 1,5-hexadiene, norbornadiene and dicyclopentadiene; dipentene; polybutadiene and copolymers containing polybutadiene blocks; butadiene based polymers and copolymers; polyisoprene and copolymers containing polyisoprene blocks; isoprene based polymers and copolymers; polyethylene; C_{4-20} α-olefins either linear or branched; styrene or divinylbenzene; ethylene-propylene rubbers and ethylene-propylene-diene rubbers; di-furnane derivatives; ester derivatives of fatty acids; and vinylpolybutadiene.

4. A polypropylene according to any one of claims 1 to 3 wherein the grafting agent comprises from 0.01 to 5 wt% of the weight of the polypropylene.

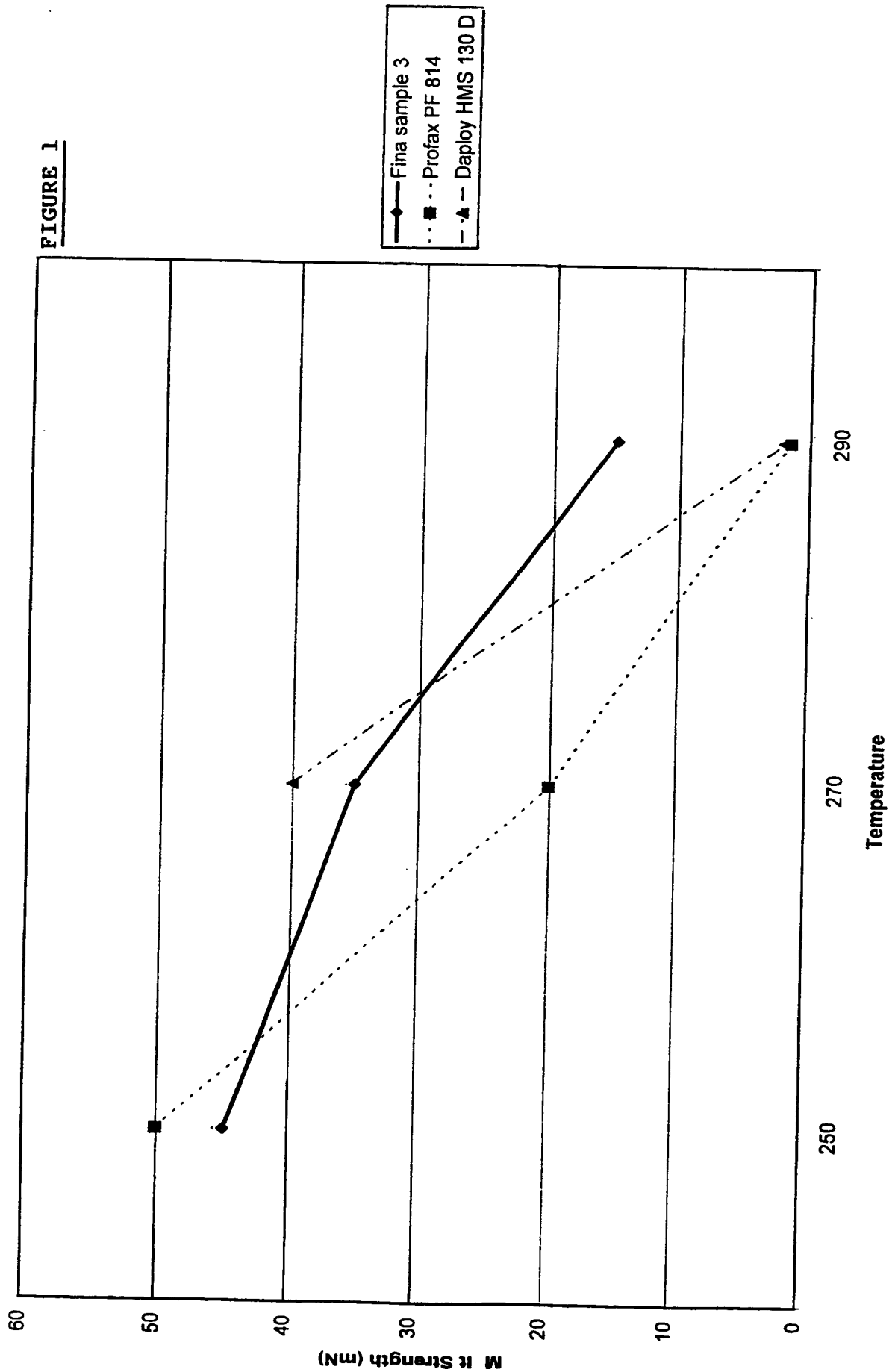
5. A polypropylene according to any one of claims 1 to 4 wherein the grafting agent comprises tetravinyl silane.

6. A polypropylene according to claim 5 wherein the tetravinyl silane is in an amount of from 0.01 to 1 wt% based on the weight of the polypropylene.

7. Polypropylene having a branching index of lower than 0.7 and an improved melt strength obtained by irradiating a polypropylene with an electron beam energy of at least 5 MeV with a radiation dose of 5 to 100 kGray in the presence of a grafting agent.

8. A process to produce a polypropylene with improved long chain branching and high melt strength in accordance with anyone of the preceding claims.

FIGURE 1


Fina sample 3
Profax PF 814
Daploy HMS 130 D
M it Strength (mN)
0
10
20
30
40
50
60
Temperature
250
270
290

INTERNATIONAL SEARCH REPORT

Int[redacted]al Application No
PCT/EP 00/02573

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F255/02 C08G81/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 5 605 936 A (FELLONI MASSIMO ET AL) 25 February 1997 (1997-02-25) cited in the application page 8, line 24-42 ---	1
A	EP 0 519 341 A (HIMONT INC) 23 December 1992 (1992-12-23) example 2 ---	1
A	EP 0 520 773 A (SEKISUI CHEMICAL CO LTD) 30 December 1992 (1992-12-30) cited in the application page 5, line 11; example 1 ---	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
1 August 2000	10/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Meulemans, R

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 792 905 A (DANUBIA PETROCHEM POLYMERE) 3 September 1997 (1997-09-03) claim 1	1

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